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FORMATION OF A LIQUATION STRUCTURE IN TITANIUM-CONTAINING ALUMINOSILICATE GLASS

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The structures of titanium-containing aluminosilicate ornamental glass were investigated by electron microscopy of different resolution, electron microanalysis, and x-ray diffraction. It was found that stable and metastable liquation of melts and glasses that results in formation of macrolayers and microphases of different composition is the cause of formation of patterned coloring. The effect of the chemical composition of the glasses on liquation processes in the investigated system was demonstrated.

Compositions and conditions were elaborated at the Institute of Geology, Karelian Science Center, Russian Academy of Sciences, for manufacture of ornamental glasses containing (%²): 30.0–55.0 SiO₂, 10.0–35.0 TiO₂, 2.0–20.0 Al₂O₃, 0.2–4.0 (Fe₂O₃ + FeO), 0.2–12.0 MgO, 5.0–25.0 CaO, 2.0–10.0 Na₂O, 0.3–4.0 K₂O (RF Patent No. 1753681). Acid and basic rocks, industrial wastes, and products of concentration of mineral resources are used as the feedstock.

The laboratory studies were conducted in melting batches in Silit furnaces in 250–500 ml crucibles in an oxidizing atmosphere; approximately 100 compositions were investigated. The batches were melted in semi-industrial conditions in furnaces operating on liquid motor fuel in 3–4 liter quartz crucibles.

A special feature of these melts is the ability to opacify on cooling below the liquidus temperature. When the melts were poured onto a metal plate and then annealed, opaque or semi-opaque materials with a fire-polished surface and patterned design in dark blue, light blue, beige, brown, lilac, and other hues were formed. The materials were x-ray-amorphous, contained no crystalline phases, and had physico-mechanical properties close to natural stone. The interesting color range and properties allow using these opaque glasses for manufacturing souvenirs, jewelry, inlaid work, fireplace finishing tiles, and interiors.

The structure of the glasses was investigated with a VEGA 11 LSM electron microscope with a microanalysis attachment and magnification by 80–210 times to determine the nature of the patterned coloring.

Two samples of glass of different color and chemical composition (see Table 1) were investigated. Sample 1 was a transparent brown matrix with a light blue, dark blue and beige design. The electron image of the structure of the glass is a light gray field (matrix) with gray and dark gray bands (Fig. 1).

The chemical composition of the bands primarily differed in the Al₂O₃ content. At a 5.48% alumina content in the glass, the amount in the matrix was 2.25%, while it varied from 6.32 to 12.95% in the bands. The SiO₂, TiO₂, and CaO content varied less, within the limits of 1–3%. The content of other oxides differed insignificantly (by no more than 0.5%).

Sample 2 consisted of a dark-brown opaque matrix with light blue bands. The electron image was a gray field with darker bands. As in the first case, the compositions of matrix and bands differed, primarily by the Al₂O₃ content (3.5% less in the matrix), and the amount of residual oxides varied less significantly (SiO₂ by 2.0%, TiO₂ by 0.8%, CaO by 0.5%).

A direct correlation between the SiO₂, TiO₂, and CaO content in the glasses and an inverse correlation was noted between Al₂O₃ and TiO₂, Al₂O₃ and SiO₂.

The data obtained were interpreted with the concepts concerning the coordination state of titanium in the structure of melts, glasses, and Sitalls [1]. In examining the catalytic effect of titanium in Sitall-forming systems, most investigators depart from the possibility of the different coordination of titanium with respect to oxygen. Six-coordination is most characteristic of Ti⁴⁺, but it is assumed that it can drop to four-coordination at high temperatures, ensuring the compatibility of the titanium with the silicon–oxygen base. The change in the coordination number of titanium on cooling of

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² Here and below, if not explicitly stated otherwise, weight content.

TABLE 1

Sample	Mass content, %								
	SiO ₂	TiO	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
Sample 1:									
glass	48.34	18.68	5.48	0.82	1.36	16.07	6.64	0.52	2.10
matrix	49.32 – 49.89	19.51 – 20.66	2.09 – 2.41	0.00 – 0.96	1.17 – 1.50	16.91 – 17.67	6.24 – 6.43	0.38 – 0.59	2.00 – 2.19
average (for 3 analyses)	49.71	19.96	2.25	–	1.38	17.16	6.39	0.49	2.10
gray bands	47.56 – 48.46	18.38 – 18.98	5.53 – 6.82	0.00 – 0.88	1.25 – 1.69	15.96 – 16.29	6.12 – 6.38	0.42 – 0.60	1.43 – 2.26
average (for 4 analyses)	48.00	18.56	6.32	–	1.45	16.09	6.22	0.49	2.00
dark gray bands	45.02 – 45.31	15.73 – 17.66	11.22 – 14.69	–	0.82 – 1.46	12.82 – 15.52	6.27 – 8.07	0.63 – 0.68	1.94 – 2.17
average (for 2 analyses)	45.16	16.69	12.95	–	1.28	14.17	7.17	0.65	2.05
Sample 2:									
glass	47.78	12.33	14.70	3.40	0.26	11.57	4.15	4.07	1.68
matrix	49.57 – 50.21	11.70 – 12.10	13.11 – 13.72	2.99 – 3.32	0.00 – 0.71	10.84 – 11.37	4.17 – 4.55	4.08 – 4.13	1.45 – 1.80
average (for 3 analyses)	49.87	11.86	13.47	3.19	–	11.12	4.38	4.09	1.61
bands	47.13 – 48.63	10.42 – 11.58	16.18 – 18.2	2.88 – 3.09	0 – 0.52	10.38 – 10.76	4.47 – 4.94	3.98 – 4.11	1.46 – 1.84
average (for 4 analyses)	47.75	11.04	16.99	2.97	–	10.65	4.77	4.05	1.64

melts and heat treatment of glasses is considered as the driving force of liquation processes in sitalization of glasses.

In our melts, some of the Ti⁴⁺ ions in four-coordination incorporated in the silicon – oxygen backbone probably limit entry of aluminum ions, since the formation of aluminum – titanium – silicate networks or skeletons is difficult — such structures are not formed in the crystal chemistry of silicates. Some of the aluminum ions are separated from the melt network with formation of liquid phases rich in alumina in comparison to most of the melt. This can be considered the main cause of stable liquation of these melts.

When the melts were abruptly cooled as a result of pouring them on metal, the liquation inhomogeneity was established as banded (ornamental) coloring of the glasses. The greatest differentiation of the composition of the bands was observed in low-alumina glass (Sample 1).

The electron microscopic data (× 20,000) show that microseparation with formation of a drop structure took place inside the macroinhomogeneities formed when the melt was cooled. Sections with a different drop size and with confluence of drops into larger aggregates were observed [2]. Such a structure is characteristic of metastable liquation and causes opacification of the glass.

Transition of part of the titanium from four- to the more characteristic six-coordination when the melt (glass) temperature decreases during pouring and annealing is probably the cause of metastable liquation. Due to the structural incompatibility of the [TiO₆] complexes with the silicon – oxygen base, Ti⁴⁺ is separated from the glass network with formation of phases rich in TiO₂.

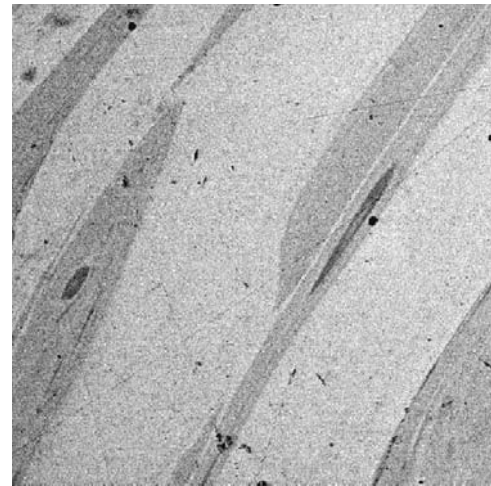


Fig. 1. Electron image of the band structure of Sample 1 (× 180).

Since liquation is a precrystallization ordering process, a conclusion can be drawn concerning the composition of the drop-shaped phases based on the data on melt crystallization in more equilibrium conditions. For this purpose, a melt of composition 1 was cooled from the liquidus temperature to room temperature at an average rate of 60 K/h. Partial crystallization was observed. According to the data from x-ray phase analysis, the crystalline phases were sphene, CaTiSiO₅, and perovskite, CaTiO₃. Based on the above, we can assume that metastable liquation goes in the direction of formation of a glass phase rich in titanium and calcium, and a phase of

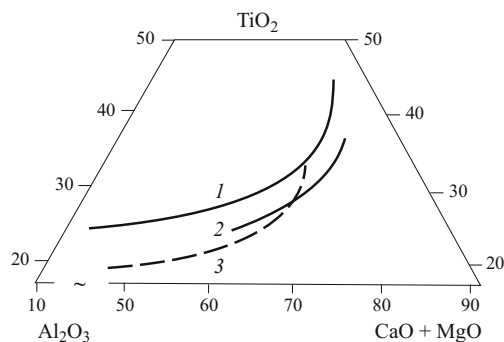


Fig. 2. Minimum titanium content in opacified glasses as a function of their composition: 1) 45–48% SiO_2 , $\text{CaO} : \text{MgO} = 2.3$; 2) 48–53% SiO_2 , $\text{CaO} : \text{MgO} = 2.3$; 3) 48–53% SiO_2 , $\text{CaO} : \text{MgO} = 5.0$.

predominantly aluminosilicate composition with low crystallizability from which crystalline phases do not separate at the given melt cooling rate.

It is necessary to note the effect of Al_2O_3 on metastable liquation in the glasses investigated. In the glass of composition 1, the matrix containing 2.25% Al_2O_3 solidifies in the form of transparent glass with no signs of opacification (liquation) on rapid cooling (pouring on metal), while bands with a higher alumina content (6.32–12.95%) liquate. At the same time, when this glass is heated a second time to 750–800°C, it opacifies over the entire volume with formation of an opaque light-beige material.

More equilibrium heat-treatment conditions are probably required for formation of a liquation structure in low-alumina glass.

In studying a wide range of compositions in this system, we found that the lower limit of the amount of TiO_2 at which opacification of the glass occurs as a result of pouring the melts onto metal decreases with an increase in the Al_2O_3 content (Fig. 2). For a relative Al^{3+} content of less than 10% (atomic) in the total amount ($\text{Al} + \text{Ti} + \text{Ca} + \text{Mg}$), opacified glasses could not be obtained.

Increasing the content of the alumina constituent in the glasses in this system thus accelerates phase separation.

The differences in the color of the bands in the glasses can be attributed to the different size of the liquation inhomogeneities. We know that titanium-containing glasses can change color as a function of the size of the titanium-containing phase — from light blue (at a high degree of dispersion) to cream-colored (with an increase in the drop size) [4].

In our case, the glasses with a high alumina content of light-blue hues (Sample 2, light blue bands in Sample 1) have a more disperse structure than low-alumina glasses (beige bands in Sample 1). This suggests that the dependence of the size of the liquation drops on the chemical composition of the glass is the cause of the ornamental coloring of the glass, sharper in low-alumina Sample 1, which consists of bands that differ significantly in the Al_2O_3 content.

Electron microscopy combined with electron microanalysis thus revealed the nature of the patterned coloring of titanium-containing aluminosilicate ornamental glasses caused by stable and metastable liquation and established the effect of the chemical composition of the glass on these processes.

The studies will facilitate selection of the compositions for manufacturing ornamental glass of defined coloring from different types of natural and technogenic raw materials.

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